15 Apr 1996

Site Affinity of Substituents in $Nd_2Fe_{17-x}T_x$ (T=Cu,Zr,Nb,Ti,V) Alloys

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In order to understand the magnetic properties of the substituted rare-earth-iron alloys, it is especially important to know the location of the substitutional atoms within the iron lattice. The site distributions of some nontransition-metal substituents in the substituted $Nd_2Fe_{17-x}T_x$ alloys have previously been reported. Here we report the site distributions of some transition-metal substituents (Cu,Zr,Nb,Ti,V) in the $Nd_2Fe_{17-x}T_x$ alloys and compare them with those of the nontransition-metal substituted compounds. Rietveld analysis of neutron powder diffraction data indicates that the nontransition-metal substituents show very similar site affinity at low substituent content. For example Al, Ga, and Si all prefer the 18*h* sites. The transition-metal substituents show a more complex site affinity. Ti and V atoms strongly prefer the 6*c* sites, Cu atoms prefer the 9*d* and 18*f* sites, Nb atoms prefer the 6*c* and 18*h* sites, and Zr atoms prefer 6*c* and 18*f* sites. It was also noted that the site affinity can change if carbon is included in the melting procedure of the sample preparation. The superconducting quantum interference device measurements show that all the substituted compounds have a Curie temperature higher than the unsubstituted parent compound. The relationship between the site distribution of substituents and the magnetic properties of the substituted $Nd_2Fe_{17-x}T_x$ alloys is discussed. [S0021-8979(96)33208-3]

INTRODUCTION

High performance permanent magnets should exhibit a Curie temperature (T_c) high enough to ensure the stability of the magnetic properties under operating conditions. Moving more and more of the iron–iron bonds into the optimum ferromagnetic exchange distance range while leaving a sufficiently concentrated iron lattice is one possible way of improving the Curie temperature of the rare-earth-iron compounds. Intensive research on enhancing the magnetic properties of the rare-earth-iron compounds by incorporation of interstitial atoms[1–6] and incorporation of substitutional atoms[7–15] (or by a combination of those two methods)[16,17] has been carried out recently.

It is well accepted that different Fe sites are of differing importance in the magnetic exchange coupling. Thus, it is especially important to know the location of substituents because new materials may be optimized by the elimination of particular exchange interactions detrimental to strong ferromagnetic interaction. The only tool capable of extracting this information directly is neutron diffraction. Analysis of the site substitution mechanism may lead to substituted compounds in which the desirable Fe–Fe bond lengths are maintained while the Fe atoms of the less desirable bonds are replaced by nonmagnetic species to give Curie temperatures high enough to be of technological interest.

We have previously reported the site distribution of some nontransition-metal substituents[6–8,14,15] in the substituted $Nd_2Fe_{17-x}T_x$ alloys. Little is known about the site distributions for most transition-metal substituents except Co.[18] The site distributions of some transition metal substituents (Cu,Zr,Nb,Ti,V) in $Nd_2Fe_{17-x}T_x$ alloys are reported. Our focus is on low substituent content because high substituent content will result in a larger reduction of magnetization.

EXPERIMENT

Samples of $Nd_2Fe_{17-x}T_x$ (T=Ti,V,Cu,Zr,Nb) were prepared from 99.9% or higher purity elements by rf induction melting in a flowing argon atmosphere at the Materials Research Center of the University of Missouri–Rolla. After melting, the ingots were wrapped in tantalum foil and were vacuum annealed at 950 °C for one week. The ingots were then crushed and ground finely in an acetone bath.

The powder neutron diffraction patterns were collected at the Missouri University Research Reactor Center by using a linear position sensitive detector with a wavelength of 1.4783 Å. The data for each sample were collected at room temperature on ~2 g of a finely powdered sample placed in a thin wall vanadium container. The two-theta range is from 5° to 105°.

Refinements of the neutron diffraction data were carried out using the program FULLPROF, which permits multiple phase refinement as well as magnetic structure refinement of each of the coexisting phases. In each of the samples, a small amount of α-Fe, ranging from 0.5% to 5% in volume, was the only detectable second phase. The Curie temperatures were measured by a superconducting quantum interference device using a Quantum Design MPMS system.

TABLE I. Site occupancies of substituents in 2:17 compounds.

Compound	Lattice parameter				χ^2	Substituent occupancies (%)				T_C (K)
	a (Å)	c (Å)	c/a	V (Å^3)		6c	9d	18f	18h	
$Nd_2Fe_{16.03}Ti_{0.97}$	8.6135(1)	12.5244(2)	1.4540	804.723	2.24	34.1	1.2	2.4	1.4	383
$Nd_2Fe_{16.03}V_{0.97}$	8.5993(2)	12.5109(4)	1.4549	801.211	1.69	38.9	0.0	3.2	0.0	365
$Nd_2Fe_{16.29}Cu_{0.71}$	8.5727(2)	12.4530(2)	1.4526	792.575	1.97	0.0	7.6	8.0	0.0	360
$Nd_2Fe_{16.12}Zr_{0.88}$	8.5903(3)	12.4730(5)	1.4520	797.100	2.24	7.8	0.0	12.0	0.0	375
$Nd_2Fe_{15.99}Nb_{1.01}$	8.5971(2)	12.4912(3)	1.4530	799.527	1.54	16.2	0.0	7.0	4.4	370
$Nd_2Fe_{15}Al_2$	8.6569(1)	12.5782(3)	1.4530	814.300	2.18	4.0	0.0	7.0	24.8	435
$Nd_2Fe_{14.8}Si_{2.2}$	8.5524(3)	12.4988(5)	1.4614	791.724	3.80	0.0	7.2	0.0	33.5	470
$Nd_2Fe_{14.9}Ga_{2.1}$	8.6281(1)	12.5531(2)	1.4549	809.304	3.34	0.0	0.0	8.8	25.6	[a]
$Nd_2Fe_{15.99}Ti_{1.01}$	8.6042(3)	12.5133(5)	1.4543	802.271	2.42	37.7	0.0	2.6	1.6	[a]
$Nd_2Fe_{15.94}Ti_{1.06}C_{0.29}$	8.6452(5)	12.4875(9)	1.4444	808.270	3.82	1.2	4.8	6.4	8.4	[a]

[a]Have not been measured.

RESULTS AND DISCUSSION

The site occupancies of the transition-metal substituents and the lattice parameters of $Nd_2Fe_{17-x}T_x$ (T=Ti, V, Cu, Zr, and Nb), obtained from neutron diffraction data, are given in Table I. For comparison, the site occupancies of some nontransition-metal substituents and their lattice parameters in $Nd_2Fe_{17-x}T_x$ (T=Al,Si,Ga), obtained in previous studies, are also given in Table I.

The unsubstituted parent compound Nd_2Fe_{17} has a unit cell volume of 799.7 Å^3. The substituents will change the unit cell volume due to the different ''size'' of different substituents and/or some other chemical/electronic effects. Previous studies showed that the nontransition-metal Al and Ga will increase the unit cell volume[6–8] while Si will decrease it.[14,16] That behavior can be explained by the ''size effect'' because Al and Ga have an atomic radius larger than that of Fe while Si has a radius smaller than that of Fe. However, the case of transition metal substitution is complex. Although most of the transition metals, such as Ti, V, Zr, and Nb, have a free atom radius much bigger than Al or Ga, the volume effect of the transition-metal substitutions are much weaker than those of the nontransition-metal substitutions. The Al or Ga expands the unit cell of Nd_2Fe_{17} compound by more than 8.5 Å^3/per substituent atom.[6–8] In contrast, the first-row transition metals Ti and V only increase the unit cell by 1.4 Å^3/V atom and 5.0 Å^3/Ti atom, respectively, while the second-row transition metals Zr and Nb even decrease the unit cell slightly (Table I). This behavior strongly suggests that the transition-metal substituents bond to Fe and Nd atoms in the 2:17 compound more strongly than do the nontransition metals.

For a singly substituted compound, the site distribution of substituents can be determined directly from the neutron diffraction data. From Table I, we see that nontransition metal substituents have a strong preference for the 18h site, which can be explained by the coordination effect, because 18h sites have the most rare earth neighbors (three) and the fewest transition neighbors (nine). Nontransition metal substituents show a preference for bonding to rare earth atoms. The transition metal substituents show more complex site affinities. For the first-row transition metals Ti, V, and Cu, the steric effect alone can be used to explain the site affinity. For the Cu compound, the small atom radius of Cu results in Cu occupancy of the 9d (which has the smallest size) and the 18f sites (which have the second smallest size). For the Ti and V compounds, the large atom radii of Ti and V force them to occupy the largest 6c sites and leave the other sites almost empty of substituents. For the second-row transition-metal substituents Zr and Nb, the site affinities of the transition-metal substituents appear to be the result of a combination of the steric effect and the coordination effect. Because they have large atom radii, the steric effect will promote occupancy of the largest 6c sites or the second largest 18h sites. However, because of their negative affinity for rare-earth neighbors, they avoid the 18h site, but take the 18f site. While Nb has a stronger affinity for the 6c site than for the 18f site, Zr shows an inverse site affinity.

Another interesting behavior which has recently been observed is also given in Table I. When carbon is included in the melt, the site affinity of Ti is totally changed. As can be seen from Table I, the Ti atoms strongly prefer the 6c sites if the sample contains no C. However, if C is introduced into the sample by melting (not the gas phase reaction method), the Ti atoms prefer the 18h and 18f sites. This phenomenon does not occur for nontransition-metal substituents.[19] A broader and deeper study of this phenomenon is underway.

The Curie temperatures of some samples were measured by a superconducting quantum interference device and the results are given in Table I. All the substituted samples have a Curie temperature higher than that of the unsubstituted parent compound Nd_2Fe_{17} (330 K) regardless of the unit cell size.

CONCLUSIONS

The nontransition-metal substituents show very similar site affinities at low substitutent content: all prefer the 18h sites. The transition-metal substituents show a more complex site affinity, e.g., Ti and V atoms prefer the 6c sites, Cu atoms prefer the 9d and 18f sites, Zr and Nb atoms prefer the 6c and 18f sites. The site affinity of the transition-metal substituent can change if carbon is included in the sample preparation by melting. All the substituted compounds have Curie temperatures higher than the unsubstituted parent compound.

ACKNOWLEDGMENTS

The authors would like to thank the Division of Materials Research of the National Science Foundation, for Grant No. DMR 9305782 and the Missouri University Research Board.

[1] D. B. de Mooij and K. H. J. Buschow, J. Less-Common Met. **142**, 349 (1988).
[2] R. B. Helmholdt and K. H. J. Buschow, J. Less-Common Met. **155**, 15 (1989).
[3] J. M. D. Coey and H. Sun, J. Magn. Magn. Mater. **87**, 1251 (1990).
[4] H. Sun, J. M. D. Coey, Y. Otani, and D. P. F. Hurley, J. Phys. Condens. Matter **2**, 6465 (1990).
[5] Y. C. Yang, X. D. Zhang, L. S. Kong, Q. Pan, J. L. Yang, Y. F. Ding, B. S. Zhang, and C. T. Ye, Solid State Commun. **78**, 313 (1991).
[6] W. B. Yelon, H. Xie, G. J. Long, O. A. Pringle, F. Grandjean, and K. H. J. Buschow, J. Appl. Phys. **73**, 6029 (1993).
[7] G. J. Long, G. K. Marasinghe, Z. Hu, W. B. Yelon, D. P. Middleton, K. H. J. Buschow, and F. Grandjean, J. Appl. Phys. **76**, 5383 (1994).
[8] Z. Hu, W. B. Yelon, S. Mishra, G. J. Long, O. A. Pringle, D. P. Middleton, K. H. J. Buschow, and F. Grandjean, J. Appl. Phys. **76**, 443 (1994).
[9] R. van Mens, J. Magn. Magn. Mater. **61**, 24 (1986).
[10] E. E. Alp, A. M. Umarji, S. K. Malik, G. K. Shenoy, M. Q. Huang, E. B. Boltich, and W. E. Wallace, J. Magn. Magn. Mater. **68**, 305 (1987).
[11] P. C. M. Gubbens, A. M. van der Kraan, T. H. Jacobs, and K. H. J. Buschow, J. Less-Common Met. **159**, 173 (1990).
[12] C. Lin, Y. X. Sun, Z. X. Liu, H. W. Jiang, G. Jiang, Y. L. Yang, B. S. Zhang, and Y. F. Ding, Solid State Commun. **81**, 299 (1992).
[13] F. Pourarian, R. Obermyer, Y. Zhang, S. G. Shankar, and W. E. Wallace, J. Appl. Phys. **73**, 6272 (1993).
[14] G. J. Long, G. K. Marasinghe, S. Mishra, O. A. Pringle, F. Grandjean, K. H. J. Buschow, D. P. Middleton, W. B. Yelon, F. Pourarian, and O. Isnard, Solid State Commun. **88**, 761 (1993).
[15] D. P. Middleton, S. Mishra, G. L. Long, O. A. Pringle, Z. Hu, W. B. Yelon, F. Grandijean, and K. H. J. Buschow, J. Appl. Phys. (to be published).
[16] W. B. Yelon, Z. Hu, E. W. Singleton, and G. C. Hadjipanayis, J. Appl. Phys. (submitted).
[17] G. K. Marasinghe, P. C. Ezekwenna, W. J. James, G. J. Long, O. A. Pringle, Z. Hu, and W. B. Yelon, these proceedings.
[18] J. Herbst, J. Croat, and W. B. Yelon, J. Appl. Phys. **53**, 250 (1982).
[19] H. Luo, Z. Hu, and W. B. Yelon (unpublished).